UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 7,186,355 B2
APPLICATION NO. : 09/777725
DATED : March 6, 2007
INVENTOR(S) : Timothy M. Swager

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Delete the title page and substitute therefor the attached title page.

In the Specification:

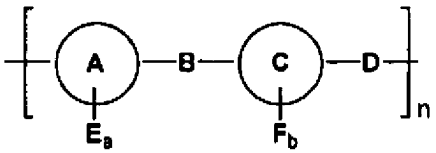
At column 1, line 10, please add the following:

-- Statement Regarding Federally Sponsored Research or Development

This invention was made with the support under the following government contract: N00014-97-1-0174 awarded by the Office of Naval Research. The government has certain rights in the invention. --

At column 8, line 27, please add the following:

-- In some embodiments, an article of the present invention may comprise a nanoscopic pathway having a conductivity, an insulating dielectric surrounding the nanoscopic pathway, and a nanoscopic switch in electronic communication with the nanoscopic pathway being capable of altering the conductivity of the nanoscopic pathway. The nanoscopic pathway may comprise a conducting polymer, wherein the conducting polymer has a structure comprising the formula:



It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

wherein A and C are aromatic groups; B and D can be a heteroatom or metal and chosen from a group of N, P, S, As, Se, or -CC-M-CC-(M=FeL_x, RuL_x, PdL_x, PtL_x, CoL_x, RhL_x, where L is neutral (phosphine, nitrogen, or π-arene based ligand) or charged (nitrogen, oxygen, or charged π-arene ligand), or are selected from the group consisting of a carbon-carbon double bond and a carbon-carbon triple bond; and any hydrogen on aromatic group A and C can be replaced by E and F respectively, wherein a and b are integers which can be the same or different and a = 0 - 4, b = 0 - 4 such that when a = 0, b is nonzero and when b = 0, a is nonzero, and at least one of E and F includes a bicyclic ring system having aromatic or non-aromatic groups optionally interrupted by O, S, NR^1 and CR^1_2 wherein R^1 is selected from the group consisting of hydrogen, C_1-C_{20} alkyl, C_1-C_{20} alkoxy and aryl and n is less than about 10,000, and wherein, when E or F is not said bicyclic ring system, E or F is a part of aromatic group A or C.

In some cases, E_a may be covalently attached to A, and the conducting polymer comprises the structure:

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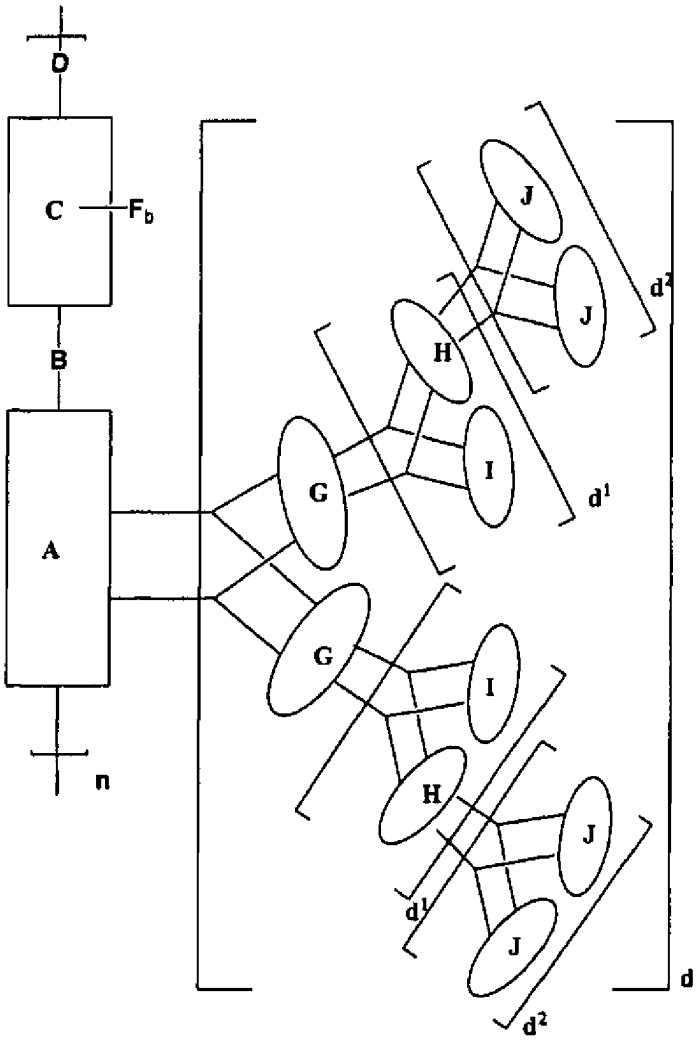
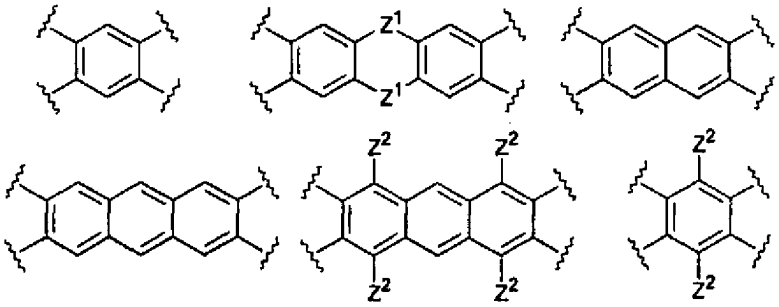
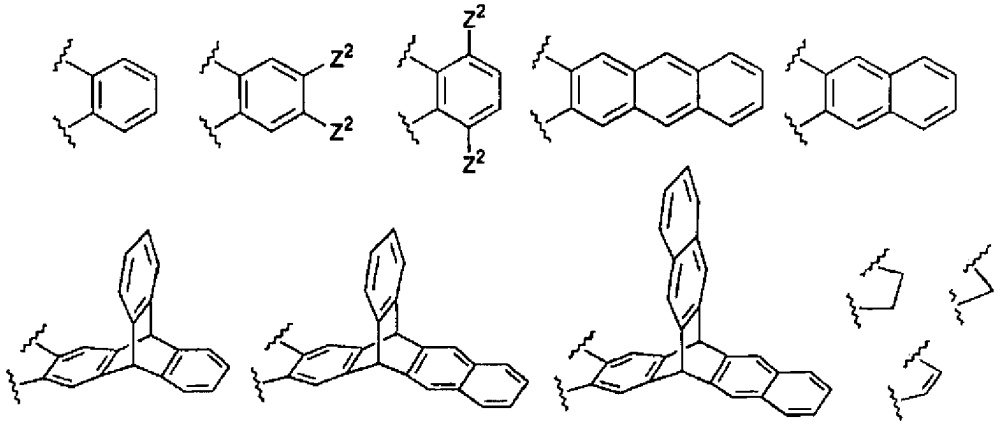


It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

wherein G, H, I, and J are aromatic groups, d = 1, 2, and d^1 = 0, 1, such that when d^1 = 0, d^2 = 0 and when d^1 = 1, d^2 = 0, 1. In some embodiments, G and H may be the same or different, and each may be selected from the group consisting of:



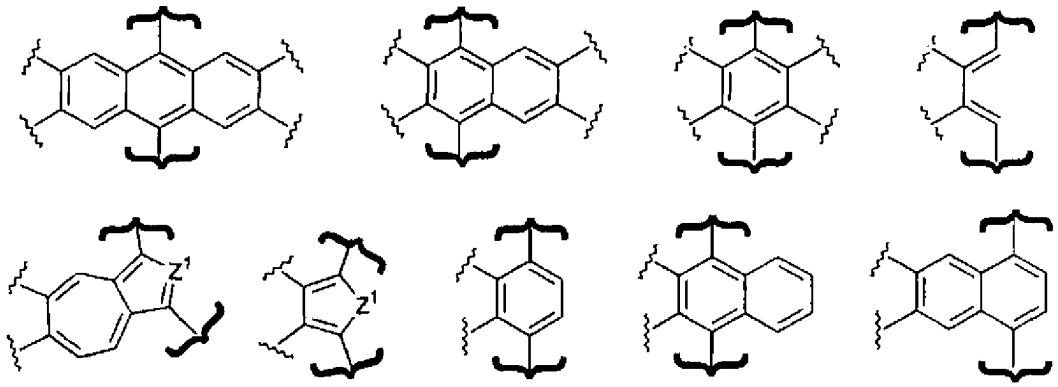
In some embodiments, I and J may be the same or different and each is selected from the group consisting of:



It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

wherein any hydrogen in G, H, I and J can be substituted by R^2, R^2 is selected from the group consisting of C_1-C_{20} alkyl, aryl, C_1-C_{20} alkoxy, phenoxy, C_1-C_{20} thioalkyl, thioaryl, $C(O)OR^3$, $N(R^3)(R^4)$, $C(O)N(R^3)(R^4)$, F, Cl, Br, I, NO_2, CN, acyl, carboxylate, hydroxy, R^3 and R^4 can be the same or different and each is selected from the group consisting of hydrogen, C_1-C_{20} alkyl, and aryl, Z^1 is selected from the group consisting of O, S and NR^8 wherein R^8 is selected from the group consisting of hydrogen, C_1-C_{20} alkyl, and aryl, and Z^2 is selected from the group consisting of F, Cl, OR^3, SR^3, NR^3R^4 and $SiR^8R^3R^4$.

In some embodiments, A may be selected from the group consisting of:



wherein any hydrogen in A can be substituted by R^5, R^5 is selected from the group consisting of C_1-C_{20} alkyl, aryl, C_1-C_{20} alkoxy, phenoxy, C_1-C_{20} thioalkyl, thioaryl, $C(O)OR^6$, $N(R^6)(R^7)$, $C(O)N(R^6)(R^7)$, F, Cl, Br, NO_2, CN, acyl, carboxylate, hydroxy; R^6 and R^7 can be the same or different and each is selected from the group consisting of hydrogen, C_1-C_{20} alkyl, and aryl; Z^1 is selected from the group consisting of O, S and NR^8

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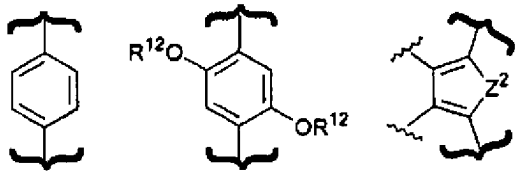
and R^8 is selected from the group consisting of hydrogen, C_1-C_{20} alkyl, and aryl; B and D can be the same or different and each is selected from the group consisting of:

wherein any hydrogen in B and D can be substituted by R^9, R^9 is selected from the group consisting of C_1-C_{20} alkyl, aryl, C_1-C_{20} alkoxy, phenoxy, C_1-C_{20} thioalkyl, thioaryl, $C(O)OR^{10}$, $N(R^{10})(R^{11})$, $C(O)N(R^{10})(R^{11})$, F, Cl, Br, NO_2, CN, acyl, carboxylate, hydroxy, R^{10} and R^{11} can be the same or different and each is selected from the group consisting of hydrogen, C_1-C_{20} alkyl, and aryl; C may be selected from the aromatic group consisting of:



wherein R^{12} is selected from the group consisting of hydrogen, C_1-C_{20} alkyl and aryl; any hydrogen in C can be substituted by F which is represented by R^{13}, R^{13} is selected from the group consisting of C_1-C_{20} alkyl, aryl, C_1-C_{20} alkoxy, phenoxy, C_1-C_{20} thioalkyl, thioaryl, $C(O)OR^{14}$, $N(R^{14})(R^{15})$, $C(O)N(R^{14})(R^{15})$, F, Cl, Br, NO_2, CN, acyl, carboxylate, hydroxy; R^{14} and R^{15} can be the same or different and each is selected from

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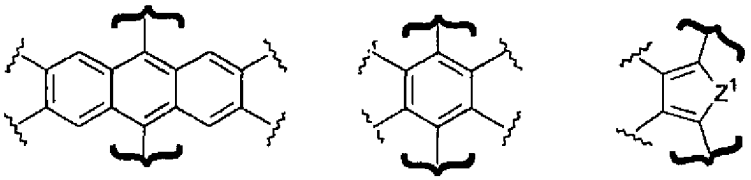
the group consisting of hydrogen, C_1-C_{20} alkyl, and aryl; Z^2 is selected from the group consisting of O, S and NR^{16} and R^{16} is selected from the group consisting of hydrogen, C_1-C_{20} alkyl, and aryl.

In one set of embodiments, A may be selected from the group consisting of:



and both B and D may be:

In the Claims, column 28, line 36, please add the following:

-- 5. The article of claim 1, wherein the conducting polymer is selected from the group consisting of polyaniline, polythiophene, polypyrrole, polyphenylene, polyarylene, poly(bisthiophene phenylene), a conjugated ladder polymer, polyiptycene, polytriphenylene, poly(arylene vinylene), poly(arylene ethynylene), and organic and transition metal derivatives thereof.

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It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

6. The article of claim 1, wherein a portion of the conducting polymer comprises a multi-dentate ligand.

7. The article of claim 1, further comprising a metal ion bonded to a portion of the conducting polymer.

8. The article of claim 1, wherein the nanoscopic pathway comprises a pathway of nanoparticles.

9. The article of claim 8, wherein the nanoparticles are selected from the group consisting of nanotubes, metal clusters, semiconductor clusters, colloids and fibers.

10. The article of claim 9, wherein the nanotubes are selected from the group consisting of carbon nanotubes and metallized nanotubes.

11. The article of claim 9, wherein the colloids are selected from the group consisting of gold colloids and silver colloids.

12. The article of claim 9, wherein the colloids comprise colloidal aggregates.

13. The article of claim 9, wherein the fibers comprise graphite.

14. The article of claim 1, wherein the nanoscopic pathway comprises a biological species.

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15. The article of claim 14, wherein the biological species is selected from the group consisting of DNA and redox-active enzymes.

16. The article of claim 1, wherein the nanoscopic pathway includes a metal ion.

17. The article of claim 16, wherein the metal ion is selected from the group consisting of transition metals, lanthanides and actinides.

18. The article of claim 16, wherein the metal ion is selected from the group consisting of iron, copper, nickel, cobalt, ruthenium, iridium, manganese, chromium, molybdenum, vanadium, uranium.

20. The article of claim 19, wherein the dielectric comprises a polymer.

21. The article of claim 20, wherein the dielectric polymer is selected from the group consisting of polyolefins, polyesters, polyamides, polyarylenes, polyethers, polyketones, polyarylsulfides, fluoropolymers, polyacrylates, polymethacrylates, polysiloxanes, polystyrene, polyurethanes, proteins and derivatives thereof.

22. The article of claim 20, wherein the dielectric polymer comprises a gel.

23. The article of claim 20, wherein the dielectric polymer is attached to the conducting polymer.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

24. The article of claim 23, wherein the dielectric polymer is attached to the conducting polymer via a chemical bond.

25. The article of claim 24, wherein the dielectric polymer is chemically bonded to the conducting polymer via a metal ion.

26. The article of claim 19, wherein the ceramic is selected from the group consisting of a metal oxide and a mixed metal oxide.

27. The article of claim 26, wherein the ceramic is a silicate.

28. The article of claim 27, wherein the silicate is a porous silicate.

29. The article of claim 1, wherein the dielectric comprises a biological species.

30. The article of claim 1, wherein the dielectric includes a metal ion.

31. The article of claim 1, wherein at least a portion of the nanoscopic pathway or the dielectric comprises a block co-polymer.

32. The article of claim 31, wherein the block co-polymer includes blocks comprising a dielectric.

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33. The article of claim 32, wherein the dielectric is selected from the group consisting of polyolefins, polyesters, polyamides, polyarylenes, polyethers, polyketones, polyarylsulfides, fluoropolymers, polyacrylates, polymethacrylates, polysiloxanes, polystyrene, polyurethanes, proteins and derivatives thereof.

34. The article of claim 31, wherein the block co-polymer includes blocks comprising a conducting material.

35. The article of claim 34, wherein the blocks comprising a conducting material is selected from the group consisting of a conjugated organic group and nanoparticles.

36. The article of claim 35, wherein the conjugated organic group is selected from the group consisting of polyaniline, polythiophene, polypyrrole, polyphenylene, polyarylene, poly(bisthiophene phenylene), a carbon ladder polymer, polyiptycene, polytriphenylene, poly(arylene vinylene), poly(arylene ethynylene), and organic and transition metal derivatives thereof.

37. The article of claim 35, wherein the nanoparticles are selected from the group consisting of nanotubes, metal clusters, colloids, and fibers.

38. The article of claim 1, wherein the dielectric is non-conducting at a first electrochemical potential range and is capable of having a resistivity of less than 10^{-4} times a resistivity at a second chemical potential.

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39. The article of claim 1, wherein the nanoscopic switch is positioned in at least a portion of the dielectric.

40. The article of claim 1, wherein the nanoscopic switch is positioned in the nanoscopic pathway.

41. The article of claim 1, wherein the nanoscopic switch and the nanoscopic pathway are capable of being redox-matched.

42. The article of claim 1, wherein the nanoscopic switch is redox-active.

43. The article of claim 1, wherein the nanoscopic switch is a metal ion.

44. The article of claim 1, wherein the nanoscopic switch comprises a biological species selected from the group consisting of DNA and a redox-active enzyme.

45. The article of claim 1, wherein the nanoscopic switch is attached to a portion of the conducting polymer.

46. The article of claim 1, wherein the nanoscopic switch is capable of being activated to alter the conductivity of the nanoscopic pathway.

47. The article of claim 46, wherein the nanoscopic switch is capable of altering the conductivity upon binding to an analyte.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

48. The article of claim 1, wherein the nanoscopic pathway is a conductor within a first electrochemical potential range.

49. The article of claim 48, wherein the nanoscopic pathway is a first nanoscopic pathway, and the dielectric comprises a second nanoscopic pathway.

50. The article of claim 49, wherein the second pathway is a conductor within a second electrochemical potential range.

51. The article of claim 50, wherein the second electrochemical potential range is greater than the first electrochemical potential range.

52. The article of claim 49, wherein the second pathway is DNA.

53. The article of claim 1, wherein the nanoscopic pathway and the nanoscopic switch are redox-matched.

54. The article of claim 53, wherein the nanoscopic pathway and the nanoscopic switch are redox-matched within a defined electrochemical potential range.

55. The article of claim 16, wherein the nanoscopic pathway and metal ion are not redox-matched when the metal ion has a first ligand environment, and wherein the nanoscopic pathway and the metal ion are redox matched when the metal ion has a second ligand environment.

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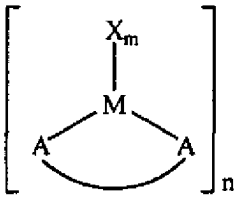
It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

56. A sensor comprising the article of claim 1, for detecting the presence of an analyte.

57. The sensor of claim 56, wherein the nanoscopic switch is a detection site for the analyte.

58. The sensor of claim 57, wherein the sensor further comprises two electrodes positioned at either end of the nanoscopic pathway.

59. The article of claim 1, wherein the conducting polymer has a structure comprising the formula:



wherein M is a metal ion, n denotes a number of monomer units, n being at least 3, the polymeric structure comprising linkages through at least one atom in 

, and 

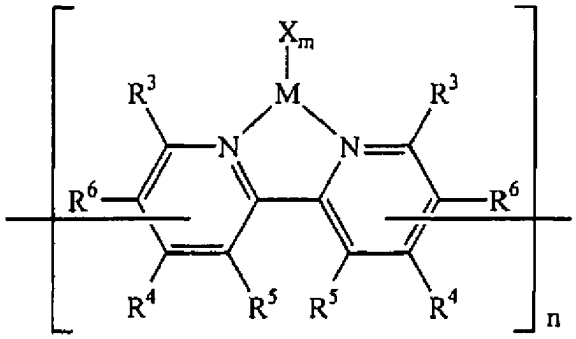
and X are selected from the group consisting of alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, cycloalkynyl, aryl, alkaryl, aralkyl and optionally interrupted or terminated by N, O, P, S, heteroalkyl, heteroaryl, carbonyl, acyl, acyloxy, —CHO, —COOR1, —CO2C(R^1)$_3$, —CONC(R^1)$_2$, cyano, nitro, alkyloxy, aryloxy, hydroxyl, hydroxyalkyl, amino, alkylamino, dialkylamino, arylamino, diarylamino,

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

—NR^1COR^2, thioalkyl, thioaryl, —SO_2R^1, —SOR^1, —SO_2OR^1, F, Cl, Br, and I; R^1 and R^2 can be the same or different, and each is selected from the group consisting of hydrogen, C1-C10 alkyl, C1-C10 heteroalkyl, aryl, heteroaryl, hydroxy, F, Cl, Br, and I, and m = 0 - 3.

60. The article of claim 4, wherein the structure comprises a 1-, 2- or 3-dimensional array of n monomer units.

61. The article of claim 1, wherein the conducting polymer has a structure comprising the formula:



wherein M is a metal ion, n denotes a number of monomer units, n being at least 3, and the polymeric structure comprises linkages through at least one of any R^3 - R^6 units or X and R^3 - R^6 can be the same or different, and each is selected from the group consisting of hydrogen, C_1-C_{10} alkyl, C_1-C_{10} heteroalkyl, aryl, heteroaryl, carbonyl, acyl, acyloxy, —CHO, —$COOR^1$, —$CO_2C(R^1)_3$, —$CONC(R^1)_2$, cyano, nitro, hydroxy, hydroxyalkyl, amino, alkylamino, dialkylamino, arylamino, diarylamino, —NR^1COR^2, thioalkyl,

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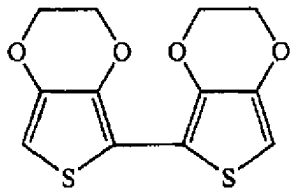
thioaryl, —SO_2R^1, —SOR^1, —SO_2OR^1, F, Cl, Br, I, or where possible, any two R groups combining to form a ring structure; R^1 and R^2 can be the same or different, and each is selected from the group consisting of hydrogen, C_1-C_{10} alkyl, C_1-C_{10} heteroalkyl, aryl, heteroaryl, hydroxy, F, Cl, Br, and I; and X is selected from the group consisting of alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, cycloalkynyl, aryl, alkaryl, aralkyl and optionally interrupted or terminated by N, O, P, S, heteroalkyl, heteroaryl, carbonyl, acyl, acyloxy, —CHO, —$COOR^1$, —$CO2C(R^1)_3$, —$CONC(R^1)_2$, cyano, alkyloxy, aryloxy, hydroxy, hydroxyalkyl, amino, alkylamino, dialkylamino, arylamino, diarylamino, —NR^1COR^2, thioalkyl, thioaryl, —SO_2R^1, —SOR^1, —SO_2OR^1, F, Cl, Br, and I; R^1 and R^2 can be the same or different, and each is selected from the group consisting of hydrogen, C_1-C_{10} alkyl, C_1-C_{10} heteroalkyl, aryl, heteroaryl, hydroxy, F, Cl, Br, and I, and m = 0 - 3.

62. The article of claim 61, wherein the structure comprises a 1-, 2- or 3-dimensional array of n monomer units.

63. The article of claim 61, wherein R3 or R6 comprises the formula:



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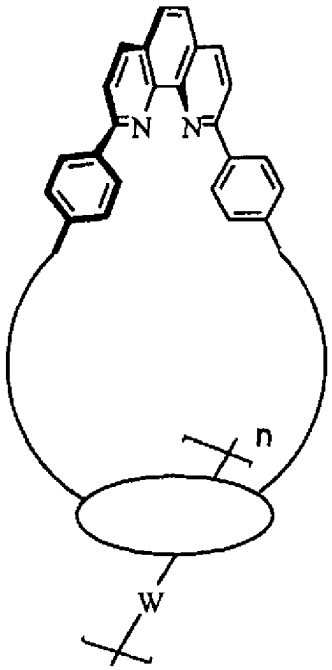
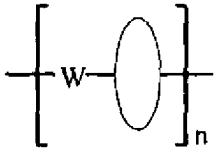
64. The article of claim 61, wherein X comprises the formula:



wherein ( ) comprises two continuous chains of atoms and 

comprises a species selected from the group consisting of a dielectric and a conductive nanoscopic pathway, and n is an integer greater than 0.

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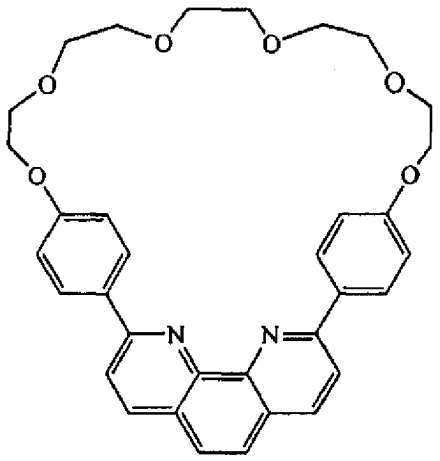
65. The article of claim 64, wherein the continuous chains of atoms comprises chains of methylene units optionally interrupted by an atom selected from the group consisting of oxygen, nitrogen, sulfur and phosphorus.

66. The article of claim 64, wherein the continuous chains comprise chains of ethylene.

67. The article of claim 1, wherein X comprises the formula:



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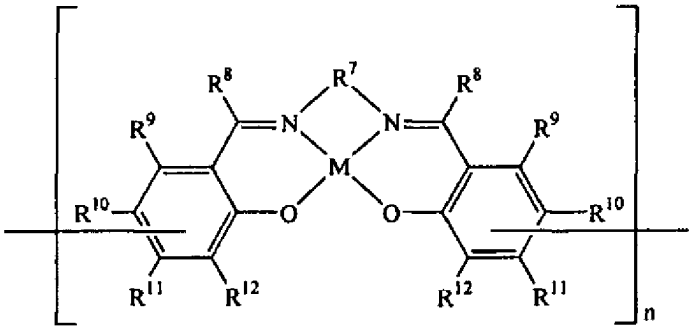
68. The article of claim 1, wherein the conducting polymer has a structure comprising the formula:



wherein M is a metal ion, n denotes a number of monomer units, n being at least 3, the polymeric structure comprising linkages through at least one atom in $R^7 - R^{12}$ units, and $R^7 - R^{12}$ can be the same or different, and each is selected from the group consisting of hydrogen, C_1-C_{10} alkyl, C_1-C_{10} heteroalkyl, aryl, heteroaryl, carbonyl, acyl, acyloxy, —CHO, —$COOR^1$, —$CO_2C(R^1)_3$, —$CONC(R^1)_2$, cyano, nitro, hydroxy, hydroxyalkyl, amino, alkylamino, dialkylamino, arylamino, diarylamino, —NR^1COR^2, thioalkyl, thioaryl, —SO_2R^1, —SOR^1, —SO_2OR^1, F, Cl, Br, and I, or where possible, any two R groups combining to form a ring structure; R^1 and R^2 can be the same or different, and each is selected from the group consisting of hydrogen, C_1-C_{10} alkyl, C_1-C_{10} heteroalkyl, aryl, heteroaryl, hydroxy, F, Cl, Br, and I.

69. The article of claim 68, wherein the structure comprises a 1-, 2- or 3-dimensional array of n monomer units.

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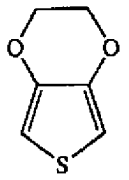
70. The article of claim 68, wherein R^{10} is:



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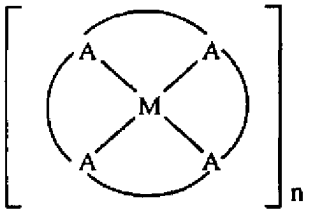
71. The article of claim 1, wherein the conducting polymer has a structure comprising the formula:



wherein M is a metal ion, n denotes a number of monomer units, n being at least 3, the polymeric structure comprising linkages through at least one atom in 

, and any 

unit or X is selected from the group consisting of alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, cycloalkynyl, aryl, alkaryl, aralkyl and optionally interrupted or terminated by N, O, P, S, heteroalkyl, heteroaryl, carbonyl, acyl, acyloxy, —CHO, —$COOR^1$, —$CO_2C(R^1)_3$, —$CONC(R^1)_2$, cyano, nitro, alkyloxy, aryloxy,

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

hydroxyl, hydroxyalkyl, amino, alkylamino, dialkylamino, arylamino, diarylamino, —NR^1COR^2, thioalkyl, thioaryl, —SO_2R^1, —SOR^1, —SO_2OR^1, F, Cl, Br, and I; R^1 and R^2 can be the same or different, and each is selected from the group consisting of hydrogen, C_1-C_{10} alkyl, C_1-C_{10} heteroalkyl, aryl, heteroaryl, hydroxy, F, Cl, Br, and I, and m = 0-2.

72. The article of claim 71, wherein the structure comprises a 1-, 2- or 3- dimensional array of n monomer units.

73. The article of claim 71, wherein the four 

units comprise a macrocycle.

74. The article of claim 73, wherein the macrocycle is selected from the group consisting of cyclams, phthalocyanines and porphyrins.

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 7,186,355 B2
APPLICATION NO. : 09/777725
DATED : March 6, 2007
INVENTOR(S) : Timothy M. Swager

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

75. The article of claim 73, wherein the metal ion is a transition metal ion. --

This certificate supersedes the Certificate of Correction issued June 9, 2009.

Signed and Sealed this

Seventh Day of July, 2009

John Doll

JOHN DOLL
Acting Director of the United States Patent and Trademark Office

(12) **United States Patent**
Swager

(10) **Patent No.: US 7,186,355 B2**
(45) **Date of Patent: Mar. 6, 2007**

(54) **INSULATED NANOSCOPIC PATHWAYS, COMPOSITIONS AND DEVICES OF THE SAME**

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(73) Assignee: **Massachusetts Institute of Technology**, Cambridge, MA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 793 days.

(21) Appl. No.: **09/777,725**

(22) Filed: **Feb. 5, 2001**

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(52) **U.S. Cl.** **252/500**; 252/502; 252/510; 252/506; 204/415; 422/98; 525/50; 257/40; 257/139

(58) **Field of Classification Search** 252/500, 252/502, 506, 510; 204/415; 422/98; 525/50; 257/40, 139

See application file for complete search history.

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(57) **ABSTRACT**

The present invention relates to compositions which provide an insulated nanoscopic pathway. The pathway comprises molecules, polymers or nanoscopic particles capable of conducting charge integrated with nanoscopic switches which are capable of electronic communication with the charge-conducting species. Turning "on" the nanoscopic switch electronically "connects" the various molecules/particles, such that a continuous nanoscopic pathway results. The nanoscopic pathway can be used in a sensor, where the switches can act as receptors for analytes. Binding of an analyte can result in a variety of effects on the nanoscopic pathway, including altering the conductivity of the nanoscopic pathway.

75 Claims, 25 Drawing Sheets